Large Kinetic Isotope Effects for the Protonolysis of Metal-Methyl Complexes Are Not Reliable Mechanistic Indicators

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Supporting Information

Contents

1. **Table of measured KIEs for the protonolysis of M-Me complexes at different temperatures using different methods.**

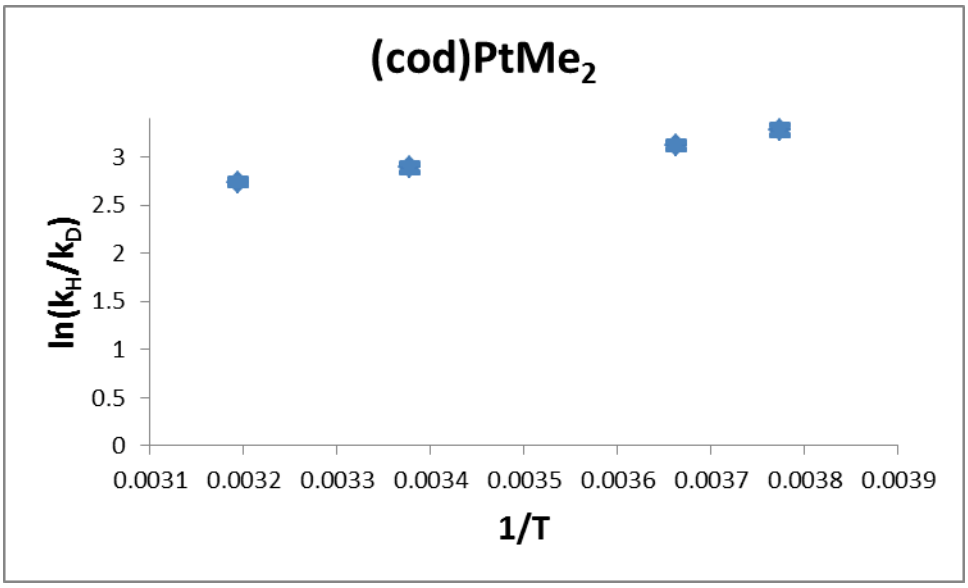
Complex	Temperature	Method	# of runs	KIE
(cod)$PtMe_2$	-8	1	7	20.8 ± 1.0
		2	4	26.7 ± 1.4
	0	1	3	20.0 ± 2.1
		2	5	22.7 ± 0.9
		3	3	22.9 ± 1.7
	23	1	4	18.0 ± 0.9
	40	1	3	16.4 ± 0.6
		2	3	15.5 ± 0.5
$^{tBu2}Cp_2ZrMe_2$	-8	1	3	11.5 ± 1.8
		2	3	10.7 ± 0.2
	0	2	3	10.4 ± 0.7
	23	1	3	10.0 ± 1.1
		2	2	10.2 ± 0.11
	40	1	8	9.2 ± 0.6
		2	6	9.6 ± 1.0

$ZnMe_2$	-8	1	3	2.2 ± 0.1
		2	3	3.4 ± 0.3
	0	2	3	3.1 ± 0.3
	23	1	3	3.1 ± 0.7
	40	2	3	2.9 ± 0.3
$(dppe)PdMe_2$ - TFA	-8	2	4	9.7 ± 0.4
	0	2	4	8.1 ± 0.8
	23	2	4	6.9 ± 0.2
	40	2	4	7.2 ± 0.2
(PONOP)RhMe	-8	1	3	6.0 ± 0.9
	0	2	3	10.5 ± 3.1
	23	1	5	6.1 ± 0.4
(PONOP)IrMe	-8	1	2	13.4 ± 0.8
	23	1	6	10.5 ± 1.1

2. General considerations for Arrhenius plots

All equations and errors of Arrhenius plots were generated using a linear least squares regression with a 95% confidence level by Matlab.

3. Arrhenius plot and equation for (cod)$PtMe_2$



cf(x) = p1*x + p2

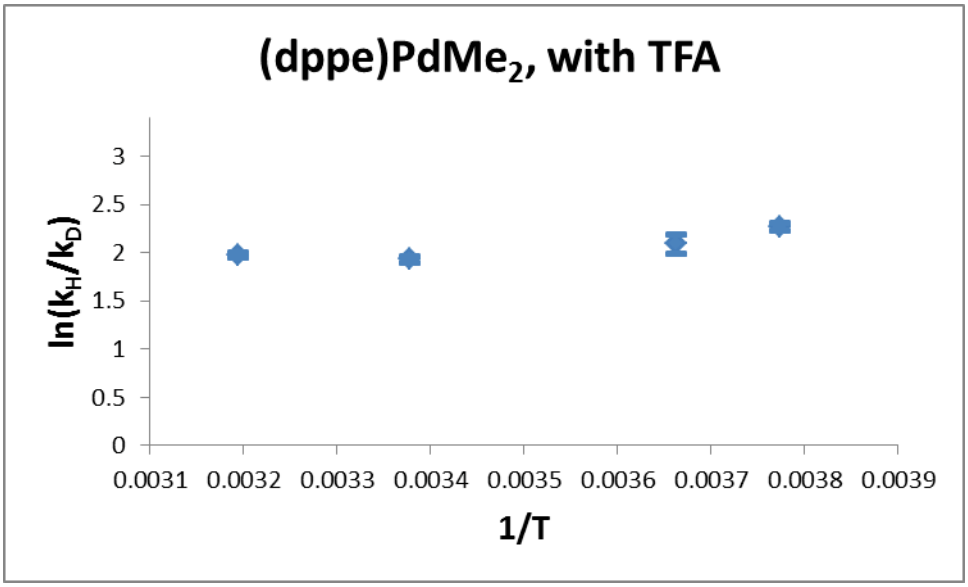
Coefficients (with 95% confidence bounds):

p1 = 856.5 (425.4, 1288)

p2 = -0.006875 (-1.535, 1.521)

goodness of fit (R squared) = 0.97337

4. Arrhenius plot and equation for (dppe)$PdMe_2$ with TFA



cf(x) = p1*x + p2

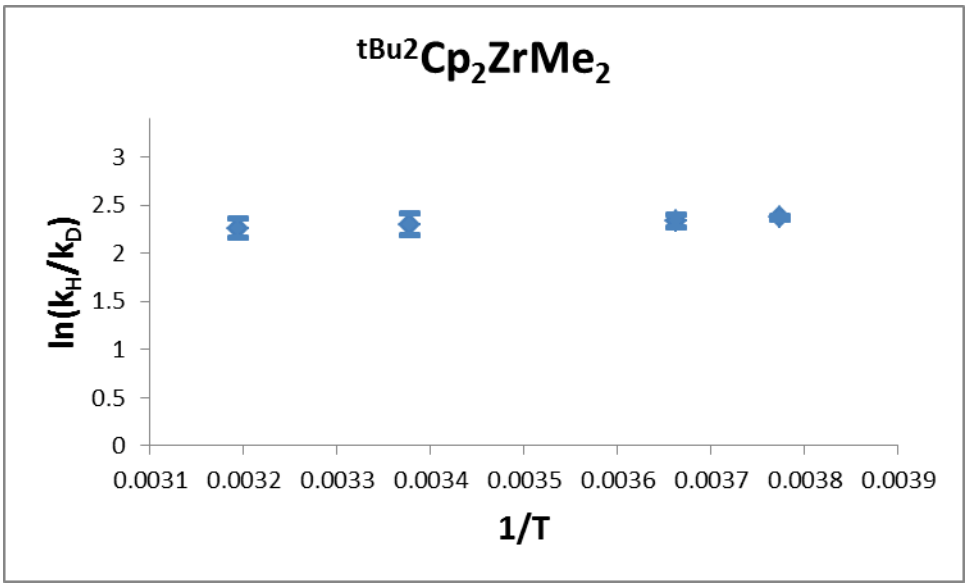
Coefficients (with 95% confidence bounds):

p1 = 479.8 (-385, 1345)

p2 = 0.3765 (-2.717, 3.47)

goodness of fit (R squared) = 0.74023

5. Arrhenius plot and equation for $^{tBu2}Cp_2ZrMe_2$



cf(x) = p1*x + p2

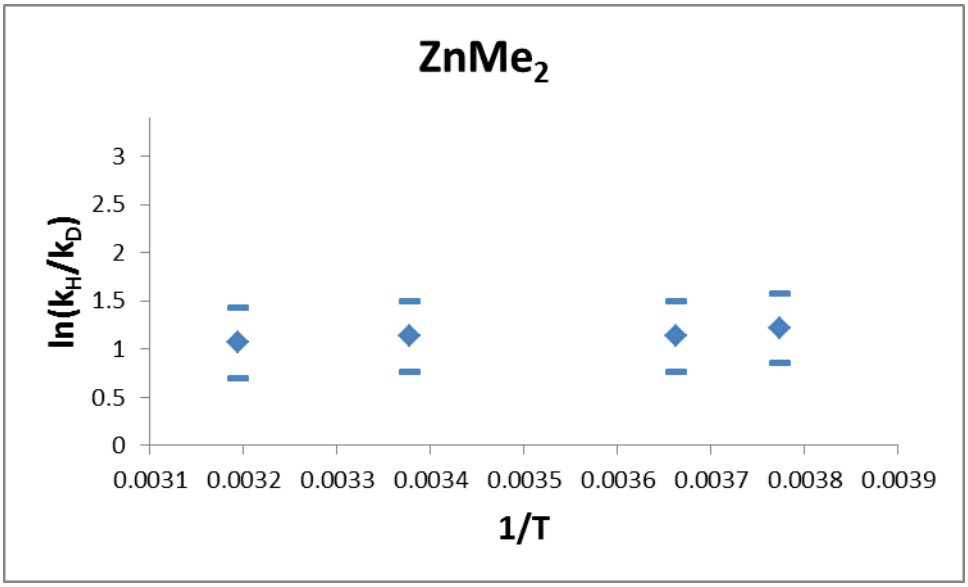
Coefficients (with 95% confidence bounds):

p1 = 172.6 (111.2, 234)

p2 = 1.714 (1.494, 1.934)

goodness of fit (R squared) = 0.98651

6. Arrhenius plot and equation for $ZnMe_2$



cf(x) = p1*x + p2

Coefficients (with 95% confidence bounds):

p1 = 178.5 (-220.2, 577.1)

p2 = 0.5181 (-0.8668, 1.903)

goodness of fit (R squared) = 0.64977

7. Table of parameters and R^2 values for Arrhenius plots for complexes

Complex	$E_a^D - E_a^H$ (kcal)	A_H/A_D	R^2
(cod)$PtMe_2$ – fixed error on reported data	3.2 ± 0.2	$0.08 \pm^{0.03}_{0.02}$	0.99715
(cod)$PtMe_2$	1.7 ± 0.9	$0.9 \pm^{3.6}_{0.8}$	0.97337
(dppe)$PdMe_2$ - fixed error on reported data using TFE	2.5 ± 0.4	$0.3 \pm^{0.3}_{0.1}$	0.99715
(dppe)$PdMe_2$ – using TFA	1.0 ± 1.7	$1.5 \pm^{34.0}_{1.4}$	0.74023
$^{tBu2}Cp_2ZrMe_2$	0.3 ± 0.1	$5.6 \pm^{1.3}_{1.1}$	0.98651
$ZnMe_2$	0.4 ± 0.8	$1.7 \pm^{5.0}_{1.3}$	0.64977